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Metallocene catalyst systems with inorganic oxides as carriers

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(54) Title: METTALLOCENE CATALYST SYSTEMS WITH INORGANIC OXIDES AS CARRIERS				
(54) Bezeichnung: METALLOCENEKATALYSATORSYSTEME MIT ANORGANISCHEN OXIDEN ALS TRÄGER				
(57) Abstract				
<p>Catalyst systems for the polymerisation of C<sub>2</sub> to C<sub>12</sub> alk-1-enes containing (A) an inorganic carrier, (B) at least one metallocene complex, (C) at least one metallocenium ion-forming compound and (D) possibly at least one metal compound of an alkaline or alkaline earth metal or a metal of the third main group of the periodic system, in which the inorganic carrier is an inorganic oxide having a pH of 1 to 6 and contains hollows and channels, of which the proportionate total macroscopic volume in the whole particle is in the range from 5 to 30 %.</p>				
(57) Zusammenfassung				
<p>Katalysatorsysteme zur Polymerisation von C<sub>2</sub>- bis C<sub>12</sub>-Alk-1-enen, enthaltend A) einen anorganischen Träger, B) mindestens einen Metallocenkomplex, C) mindestens eine metalloceniumionenbildende Verbindung und D) gegebenenfalls mindestens eine organische Metallverbindung eines Alkali- oder Erdalkalimetalls oder eines Metalls der III. Hauptgruppe des Periodensystems, wobei als anorganischer Träger ein anorganisches Oxid verwendet wird, welches einen pH-Wert von 1 bis 6 und Hohlräume und Kanäle aufweist, deren makroskopischer Volumenanteil am Gesamtpartikel im Bereich von 5 bis 30 % liegt.</p>				

Metallocene catalyst systems having inorganic oxides as supports

5 Abstract

In catalyst systems for polymerizing C<sub>2</sub>-C<sub>12</sub>-alk-1-enes, comprising

- 10 A) an inorganic support,
- B) at least one metallocene complex,
- 15 C) at least one compound capable of forming metallocenium ions and
- D) if desired, at least one organic metal compound of an alkali metal or alkaline earth metal or a metal of main group III of the Periodic Table,

20 the inorganic support used is an inorganic oxide which has a pH of from 1 to 6 and voids and channels whose macroscopic proportion by volume based on the total particle is in the range from 5 to 30 %.

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Metallocene catalyst systems having inorganic oxides as supports

- 5 The present invention relates to catalyst systems for polymerizing C<sub>2</sub>-C<sub>12</sub>-alk-1-enes, comprising
- A, an inorganic support,
  - 10 B, at least one metallocene complex,
  - C, at least one compound capable of forming metallocenium ions and
  - 15 D, if desired, at least one organic metal compound of an alkali metal or alkaline earth metal or a metal of main group III of the Periodic Table,
- 20 wherein the inorganic support used is an inorganic oxide which has a pH of from 1 to 6 and voids and channels whose macroscopic proportion by volume based on the total particle is in the range from 5 to 30 %.
- 25 Furthermore, the present invention relates to a process for preparing polymers of C<sub>2</sub>-C<sub>12</sub>-alk-1-enes with the aid of these catalyst systems, the polymers obtainable in this way and also films, fibers and molds of these polymers.
- 30 Metallocene catalysts are complexes of transition metals with organic ligands which in combination with compounds capable of forming metallocenium ions give an effective catalyst system. They allow the preparation of new types of polyolefins. For commercial utilization of such metallocene catalysts in current
- 35 industrial processes, it is usually necessary to apply the catalyst to a support since this gives polymers having an improved morphology, as described in EP-A 294 942. Supports used are frequently inorganic or organic oxides. The productivity of the supported metallocene catalysts is still unsatisfactory.
- 40
- Inorganic oxides such as silica gel (SiO<sub>2</sub>), are also used in propylene polymerization by means of Ziegler-Natta catalyst systems (US-A 4 857 613, US-A 5 288 824). The resulting propylene
- 45 polymers can be prepared with a quite high productivity but usually have a broad molar mass distribution and, in addition,



still have disadvantages such as nonuniform incorporation of comonomers.

5 It is an object of the present invention to develop catalyst systems for polymerizing  $C_2-C_{12}$ -alk-1-enes which lead to polymers of  $C_2-C_{12}$ -alk-1-enes having a narrow molar mass distribution, which do not have the disadvantages indicated and which are obtained with high productivity.

10 We have found that this object is achieved by catalyst systems for polymerizing  $C_2-C_{12}$ -alk-1-enes, comprising

A, an inorganic support,

15 B, at least one metallocene complex,

C, at least one compound capable of forming metallocenium ions and

20 D, if desired, at least one organic metal compound of an alkali metal or alkaline earth metal or a metal of main group III of the Periodic Table

25 wherein,

the inorganic support used is an inorganic oxide which has a pH of from 1 to 6 and voids and channels whose macroscopic  
30 proportion by volume based on the total particle is in the range from 5 to 30 %.

We have also found a process for preparing polymers of  $C_2-C_{12}$ -alk-1-enes, the resulting polymers and their use as fibers,  
35 films and moldings.

The catalyst system of the present invention is used for the polymerization of  $C_2-C_{12}$ -alk-1-enes. Preferred  $C_2-C_{12}$ -alk-1-enes  
40 are ethylene, propylene, 1-butene, 1-pentene, 4-methyl-pent-1-ene, 1-hexene, 1-heptene and 1-octene and also mixtures of these. Particular preference is given to homopolymers or copolymers of propylene and ethylene, where the proportion of ethylene or of propylene in the copolymers is at least 50 mol%.  
45 Among the copolymers of propylene, preference is given to those comprising ethylene or 1-butene or mixtures thereof as further monomers. In the case of the copolymers of ethylene, particular preference is given to those copolymers comprising propylene or



1-butene or 1-hexene or 1-octene or mixtures thereof as further monomers.

5 Preference is given to using the catalyst systems of the present invention for preparing polymers comprising

from 50 to 100 mol% of propylene,  
from 0 to 50 mol%, in particular from 0 to 30 mol%, of ethylene  
10 and  
from 0 to 20 mol%, in particular from 0 to 10 mol%, of  
C<sub>4</sub>-C<sub>12</sub>-alk-1-enes.

15 Preference is also given to polymers comprising

from 50 to 100 mol% of ethylene,  
from 0 to 50 mol%, in particular from 0 to 30 mol%, of propylene  
and  
20 from 0 to 50 mol%, in particular from 0 to 30 mol%, of  
C<sub>4</sub>-C<sub>12</sub>-alk-1-enes.

The sum of these mol% figures is always 100.

25 The polymerization using the catalyst systems of the present invention is carried out at from -50 to 300°C, preferably from 0 to 150°C, and at pressures of from 0.5 to 3000 bar, preferably from 1 to 80 bar. In this process, which is likewise subject  
30 matter of the present invention, the residence times of the respective reaction mixtures should be set to from 0.5 to 5 hours, in particular from 0.7 to 3.5 hours. The polymerization can also be carried out in the presence of, inter alia, antistatic agents and molar mass regulators, for example hydrogen.

35 The polymerization can be carried out in solution, in suspension, in liquid monomers or in the gas phase. The polymerization is preferably carried out in liquid monomers or in the gas phase, with the stirred gas phase being preferred.

40 The process of the invention can be carried out either continuously or batchwise. Suitable reactors are, inter alia, continuously operated stirred reactors; it is here also possible to employ a plurality of stirred reactors connected in series  
45 (reactor cascade).



The catalyst systems of the present invention comprise an inorganic support as component A<sub>1</sub>. The inorganic support used is an inorganic oxide which has a pH, determined by the method of S.R. Morrison, "The Chemical Physics of Surfaces", Plenum Press, New York [1977], page 130ff, of from 1 to 6 and voids and channels whose macroscopic proportion by volume based on the total particle is in the range from 5 to 30 %. Preference is here given to using, in particular, those inorganic oxides whose pH, i.e. the negative logarithm to the base 10 of the proton concentration, is in the range from 2 to 5.5 and in particular in the range from 2 to 5. Furthermore, inorganic supports used are, in particular, those inorganic oxides which have voids and channels whose macroscopic proportion by volume based on the total particle is from 8 to 30 %, preferably from 10 to 30 % but particularly preferably from 15 to 25 %.

Inorganic supports used are also, in particular, those inorganic oxides which have a mean particle diameter of from 5 to 200  $\mu\text{m}$ , in particular from 20 to 90  $\mu\text{m}$ , and a mean particle diameter of the primary particles of from 1 to 20  $\mu\text{m}$ , in particular from 1 to 5  $\mu\text{m}$ . These primary particles are porous granular particles. The primary particles contain pores having a diameter of, in particular, from 1 to 1000 Å. Furthermore, the inorganic oxides to be used according to the present invention also contain voids and channels having a mean diameter of from 0.1 to 20  $\mu\text{m}$ , in particular from 1 to 15  $\mu\text{m}$ . The inorganic oxides also have, in particular, a pore volume of from 0.1 to 10  $\text{cm}^3/\text{g}$ , preferably from 1.0 to 5.0  $\text{cm}^3/\text{g}$ , and a specific surface area of from 10 to 1000  $\text{m}^2/\text{g}$ , preferably from 100 to 500  $\text{m}^2/\text{g}$ .

Owing to the voids and channels present in the finely divided inorganic oxides, the active catalyst components have a significantly improved distribution in the support material. The acid centers on the surface of the inorganic oxide additionally effect a homogeneous loading with the catalyst constituents. Furthermore, such a material pervaded by voids and channels has a positive effect on the diffusion-controlled supply of monomers and cocatalysts and thus on the polymerization kinetics.

Such a finely divided inorganic oxide can be obtained, for example, by spray drying of milled, appropriately sieved hydrogels which for this purpose are slurried with water or an aliphatic alcohol. During spray drying, the required pH of from 1 to 6 can also be set by use of appropriately acid primary particle suspensions. However, such a finely divided inorganic oxide is also commercially available.



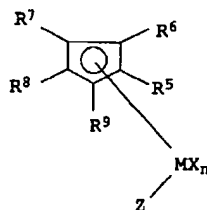
## 5

Preferred inorganic supports are, in particular, oxides of silicon, aluminum, titanium or one of the metals of main group I or II of the Periodic Table. Besides aluminum oxide or magnesium oxide or a sheet silicate, the inorganic oxide used is very particularly preferably silica gel ( $\text{SiO}_2$ ) which can be obtained, in particular by spray drying.

Components A<sub>1</sub> used can also be cogels, i.e. mixtures of at least two different inorganic oxides.

Preference is given to using from 0.1 to 10000  $\mu\text{mol}$ , in particular from 5 to 200  $\mu\text{mol}$ , of the metallocene complex, i.e. the component B<sub>1</sub>, per gram of support, i.e. the component A<sub>1</sub>.

As component B<sub>1</sub>, one or more metallocene complexes are present in the catalyst system of the present invention. Suitable metallocene complexes are particularly those of the general formula IV



IV

where the substituents have the following meanings:

M is titanium, zirconium, hafnium, vanadium, niobium or tantalum, or an element of transition group III of the Periodic Table and the lanthanides,

X is fluorine, chlorine, bromine, iodine, hydrogen,  $\text{C}_1\text{-C}_{10}$ -alkyl,  $\text{C}_6\text{-C}_{15}$ -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical,  $-\text{OR}^{10}$  or  $-\text{NR}^{10}\text{R}^{11}$ ,

n is an integer from 1 to 3, with n corresponding to the valence of M minus the number 2,



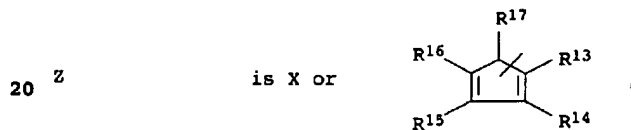


where

5  $R^{10}$  and  $R^{11}$  are  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{15}$ -aryl, alkylaryl, aryl-alkyl, fluoroalkyl or fluoroaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical,

10  $R^5$  to  $R^9$  are hydrogen,  $C_1$ - $C_{10}$ -alkyl, 5- to 7-membered cycloalkyl which in turn bear a  $C_1$ - $C_{10}$ -alkyl as substituent,  $C_6$ - $C_{15}$ -aryl or arylalkyl, where two adjacent radicals together may also be a saturated or unsaturated cyclic group having from 4 to 15 carbon atoms, or  $Si(R^{12})_3$ , where

15  $R^{12}$  is  $C_1$ - $C_{10}$ -alkyl,  $C_3$ - $C_{10}$ -cycloalkyl or  $C_6$ - $C_{15}$ -aryl,



where the radicals

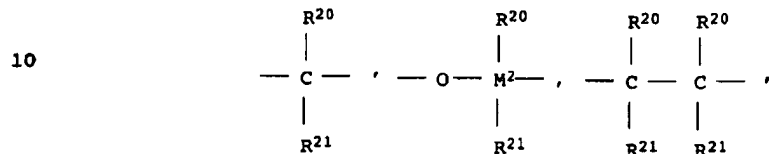
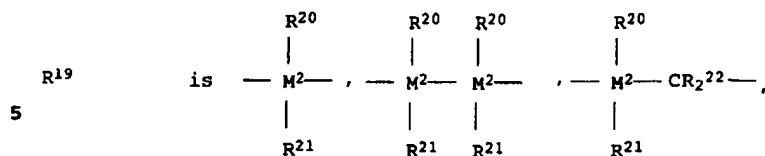
25  $R^{13}$  to  $R^{17}$  are hydrogen,  $C_1$ - $C_{10}$ -alkyl, 5- to 7-membered cycloalkyl which can in turn bear a  $C_1$ - $C_{10}$ -alkyl as substituent,  $C_6$ - $C_{15}$ -aryl or arylalkyl and where two adjacent radicals together may also be a saturated or unsaturated cyclic group having from 4 to 15 carbon atoms, or  $Si(R^{18})_3$  where

30  $R^{18}$  is  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{15}$ -aryl or  $C_3$ - $C_{10}$ -cycloalkyl,  
35 or where the radicals  $R^8$  and 2 together form a group  $-R^{19}-A-$  where

40

45





15  $= BR^{20}, = AlR^{20}, -Ge-, -Sn-, -O-, -S-, = SO, = SO_2, = NR^{20}, = CO,$   
 $= PR^{20}$  or  $= P(O)R^{20},$

where

20  $R^{20}, R^{21}$  and  $R^{22}$  are identical or different and are each a  
hydrogen atom, a halogen atom, a  $C_1$ - $C_{10}$ -alkyl  
group, a  $C_1$ - $C_{10}$ -fluoroalkyl group, a  
25  $C_6$ - $C_{10}$ -fluoroaryl group, a  $C_6$ - $C_{10}$ -aryl group, a  
 $C_1$ - $C_{10}$ -alkoxy group, a  $C_2$ - $C_{10}$ -alkenyl group, a  
 $C_7$ - $C_{40}$ -arylalkyl group, a  $C_8$ - $C_{40}$ -arylalkenyl group  
or a  $C_7$ - $C_{40}$ -alkylaryl group or two adjacent  
radicals together with the atoms connecting them  
form a ring and

30  $M^2$  is silicon, germanium or tin,

35 A is  $-O-$ ,  $-S-$ ,  $>NR^{23}$  or  $>PR^{23}$ , where

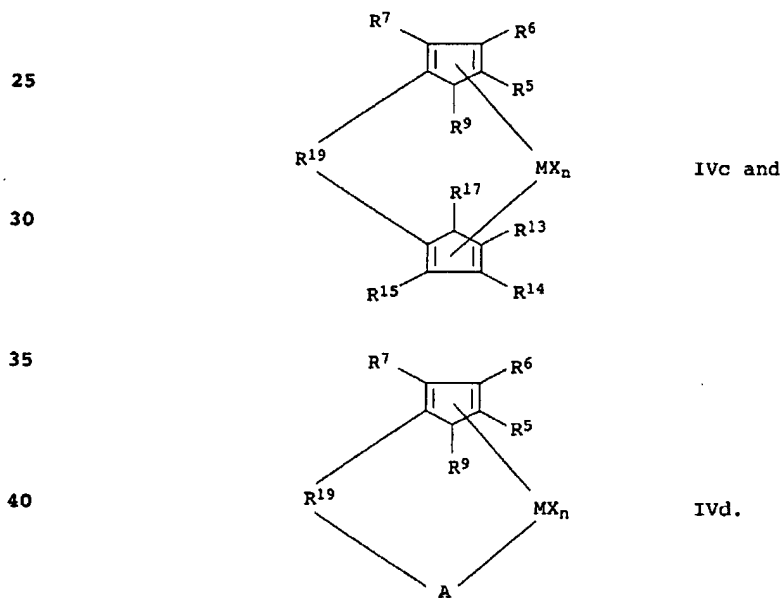
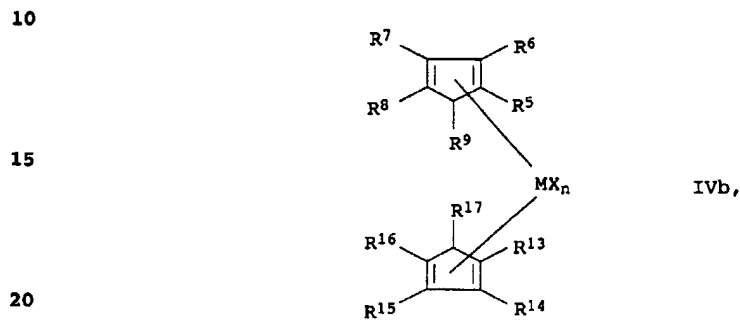
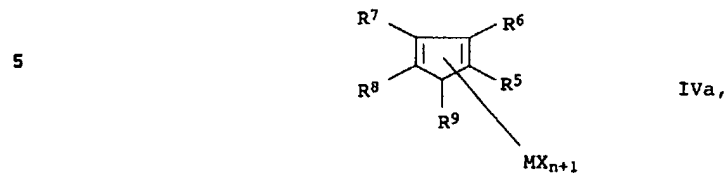
$R^{23}$  is  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{15}$ -aryl,  $C_3$ - $C_{10}$ -cycloalkyl,  
alkylaryl or  $Si(R^{24})_3$ ,

40  $R^{24}$  is hydrogen,  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{15}$ -aryl, which may  
in turn be substituted by  $C_1$ - $C_4$ -alkyl groups, or  
 $C_3$ - $C_{10}$ -cycloalkyl

45 or where the radicals  $R^8$  and  $R^{16}$  together form a group  $-R^{19}-$ .



Preferred metallocene complexes of the general formula IV are



45 The radicals x can be identical or different, preferably identical.



Among the compounds of the formula Iva, particular preference is given to those in which

- 5 M is titanium, zirconium or hafnium,  
 X is chlorine, C<sub>1</sub>-C<sub>4</sub>-alkyl or phenyl,  
 n is 2 and  
 10 R<sup>5</sup> to R<sup>9</sup> are hydrogen or C<sub>1</sub>-C<sub>4</sub>-alkyl.

Among the compounds of the formula IVb, preference is given to those in which

- 15 M is titanium, zirconium or hafnium,  
 X is chlorine, C<sub>1</sub>-C<sub>4</sub>-alkyl or phenyl,  
 20 n is 2,  
 R<sup>5</sup> to R<sup>9</sup> are hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or Si(R<sup>12</sup>)<sub>3</sub>,  
 25 R<sup>13</sup> to R<sup>17</sup> are hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or Si(R<sup>18</sup>)<sub>3</sub>.

Particularly suitable compounds are those of the formula IVb in which the cyclopentadienyl radicals are identical.

- 30 Examples of particularly suitable compounds are:  
 bis(cyclopentadienyl)zirconium dichloride,  
 bis(pentamethylcyclopentadienyl)zirconium dichloride,  
 bis(methylcyclopentadienyl)zirconium dichloride,  
 35 bis(ethylcyclopentadienyl)zirconium dichloride,  
 bis(n-butylcyclopentadienyl)zirconium dichloride and  
 bis(trimethylsilylcyclopentadienyl)zirconium dichloride  
 and also the corresponding dimethylzirconium compounds.

- 40 Particularly suitable compounds of the formula IVc are those in which

- R<sup>5</sup> and R<sup>13</sup> are identical and are hydrogen or C<sub>1</sub>-C<sub>10</sub>-alkyl,  
 45



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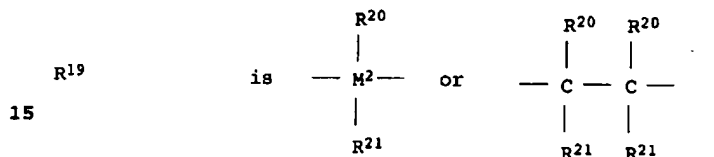
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R<sup>9</sup> and R<sup>17</sup> are identical and are hydrogen, methyl, ethyl, isopropyl or tert-butyl,

R<sup>6</sup>, R<sup>7</sup>, R<sup>14</sup> and R<sup>15</sup> have the meanings:

5 R<sup>7</sup> and R<sup>15</sup> are C<sub>1</sub>-C<sub>4</sub>-alkyl  
R<sup>6</sup> and R<sup>14</sup> are hydrogen  
or two adjacent radicals R<sup>6</sup> and R<sup>7</sup> or R<sup>14</sup> and R<sup>15</sup>  
are together a cyclic group having from 4 to 12  
carbon atoms,

10



M is titanium, zirconium or hafnium and

20

X is chlorine, C<sub>1</sub>-C<sub>4</sub>-alkyl or phenyl.

Examples of particularly suitable complexes are:

25 dimethylsilanediylbis(cyclopentadienyl)zirconium dichloride,  
dimethylsilanediylbis(indenyl)zirconium dichloride,  
dimethylsilanediylbis(tetrahydroindenyl)zirconium dichloride,  
ethylenebis(cyclopentadienyl)zirconium dichloride,  
ethylenebis(indenyl)zirconium dichloride,  
ethylenebis(tetrahydroindenyl)zirconium dichloride,  
30 tetramethylethylene-9-fluorenylcyclopentadienylzirconium  
dichloride,  
dimethylsilanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)  
zirconium dichloride,  
dimethylsilanediylbis(-3-tert-butyl-5-ethylcyclopentadienyl)  
35 zirconium dichloride,  
dimethylsilanediylbis(-2-methylindenyl)zirconium dichloride,  
dimethylsilanediylbis(-2-isopropylindenyl)zirconium dichloride,  
dimethylsilanediylbis(-2-tert-butylindenyl)zirconium dichloride,  
diethylsilanediylbis(-2-methylindenyl)zirconium dibromide,  
40 dimethylsilanediylbis(-3-methyl-5-methylcyclopentadienyl)  
zirconium dichloride,  
dimethylsilanediylbis(-3-ethyl-5-isopropylcyclopentadienyl)  
zirconium dichloride,  
dimethylsilanediylbis(-2-ethylindenyl)zirconium dichloride,  
45 dimethylsilanediylbis(-2-methylbenzindenyl)zirconium dichloride,  
dimethylsilanediylbis(2-ethylbenzindenyl)zirconium dichloride,  
methylphenylsilanediylbis(2-ethylbenzindenyl)zirconium



dichloride,  
 methylphenylsilanediylbis(2-methylbenzindenyl)zirconium  
 dichloride,  
 diphenylsilanediylbis(2-methylbenzindenyl)zirconium dichloride,  
 5 diphenylsilanediylbis(2-ethylbenzindenyl)zirconium dichloride,  
 and diphenylsilanediylbis(-2-methylindenyl)-hafnium dichloride  
 and also the corresponding dimethylzirconium compounds.

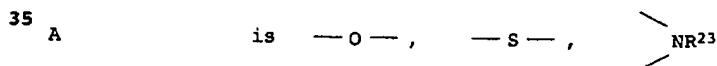
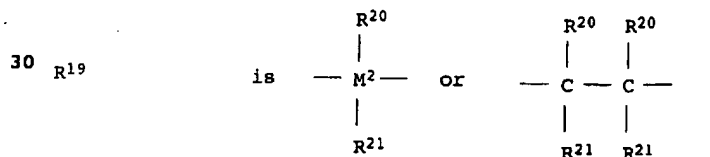
Further examples of suitable complexes are:

- 10 dimethylsilanediylbis(-2-methyl-4-phenylindenyl)zirconium  
 dichloride,  
 dimethylsilanediylbis(-2-methyl-4-naphthylindenyl)zirconium  
 dichloride,  
 dimethylsilanediylbis(-2-methyl-4-isopropylindenyl)zirconium  
 15 dichloride and  
 dimethylsilanediylbis(-2-methyl-4,6-diisopropylindenyl)zirconium  
 dichloride and also the corresponding dimethylzirconium  
 compounds.

- 20 Among the compounds of the general formula IVd, particularly  
 suitable compounds are those in which

M is titanium or zirconium,

- 25 X is chlorine, C<sub>1</sub>-C<sub>4</sub>-alkyl or phenyl,



and

- 40 R<sup>5</sup> to R<sup>7</sup> and R<sup>9</sup> are hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>3</sub>-C<sub>10</sub>-cycloalkyl,  
 C<sub>6</sub>-C<sub>15</sub>-aryl or Si(R<sup>12</sup>)<sub>3</sub> or two adjacent radicals  
 form a cyclic group having from 4 to 12 carbon  
 atoms.



The synthesis of such complexes can be carried out by methods known per se, with preference being given to reacting the corresponding substituted, cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum.

- 5 Examples of corresponding preparative methods are described, inter alia, in Organometallic Chemistry, 369 (1989), 359-370.

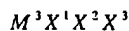
It is also possible to use mixtures of various metallocene complexes.

The catalyst system of the present invention comprises a compound capable of forming metallocenium ions as component C<sub>1</sub>.

- 10 Suitable compounds capable of forming metallocene ions are at least one compound capable of forming metallocenium ions selected from the group consisting of strong, uncharged Lewis acids, ionic compounds having Lewis-acid cations and ionic compounds having Brønsted acids as cation.

As strong, uncharged Lewis acids, preference is given to compounds of

- 15 the general formula V



V

where

M<sup>3</sup> is an element of main group III of the Periodic Table, in particular B, Al or Ga, preferably B,

- 20 X<sup>1</sup>, X<sup>2</sup> and X<sup>3</sup>

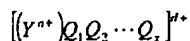
are hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical or fluorine, chlorine, bromine or iodine, in particular haloaryls, preferably pentafluorophenyl.

- 25 Particular preference is given to compounds of the general formula V in

which X<sup>1</sup>, X<sup>2</sup> and X<sup>3</sup> are identical, preferably tris(pentafluorophenyl) borane.

Suitable ionic compounds having Lewis-acid cations are those containing cations of the general formula VI

30



VI



where

- Y is an element of the main group I to VI or transition group I to VIII of the Periodic Table,
- Q<sub>1</sub> to Q<sub>2</sub> are monovalent radicals such as C<sub>1</sub>-C<sub>28</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, alkylaryl, arylalkyl, haloalkyl, haloaryl each having from 6 to 20 carbon atoms in the aryl radical and from 1 to 28 carbon atoms in the alkyl radical, unsubstituted or C<sub>1</sub>-C<sub>10</sub>-alkyl-substituted C<sub>3</sub>-C<sub>10</sub>-cycloalkyl, halogen, C<sub>1</sub>-C<sub>28</sub>-alkoxy, C<sub>6</sub>-C<sub>15</sub>-aryloxy, silyl- or mercaptyl groups,
- a is an integer from 1 to 6 and
- z is an integer from 0 to 5,
- d corresponds to the difference a-z but is greater than or equal to 1.

Particularly suitable cations are carbonium cations, oxonium cations and sulfonium cations and also cationic transition metal complexes. Particular mention may be made of the triphenylmethyl cation, the silver cation and the 1,1'-dimethylferrocenyl cation. The compounds preferably have non-coordinating counter ions, in particular boron compounds as are also mentioned in WO 91/09882, preferably tetrakis(pentafluorophenyl)borate.

Ionic compounds having Brönsted acids as cations and preferably likewise non-coordinating counter ions are mentioned in WO 91/09882. The preferred cation is N,N-dimethylanilinium.

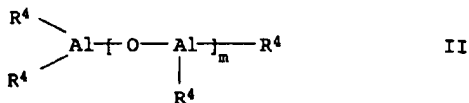
The amount of compounds capable of forming metallocenium ions is preferably from 0.1 to 10 equivalents, based on the metallocene complex IV.

Particularly suitable compounds C, capable of forming metallocenium ions are open-chain or cyclic aluminoxane compounds of the general formula II or III

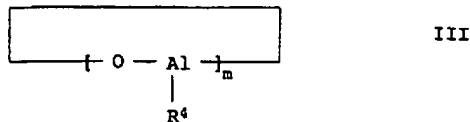




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where  $R^4$  is a  $C_1$ - $C_4$ -alkyl group, preferably a methyl or ethyl group, and  $m$  is an integer from 5 to 30, preferably from 10 to 25.

15

The preparation of these oligomeric aluminosiloxane compounds is usually carried out by reacting a solution of trialkylaluminum with water and is described, for example, in EP-A 284 708 and US A 4,794,096.

20

In general, the resulting oligomeric aluminosiloxane compounds are in the form of mixtures of linear and cyclic chain molecules having various lengths, so that  $m$  is to be regarded as a mean value. The aluminosiloxane compounds can also be present in admixture with other metal alkyls, preferably with aluminum alkyls.

25

Both the metallocene complexes (component B) and the compounds capable of forming metallocenium ions (component C) are preferably used in solution, with particular preference being given to aromatic hydrocarbons having from 6 to 20 carbon atoms, in particular xylenes and toluene.

30

As component C, it is also possible to use aryloxyaluminosiloxanes as described in US-A 5,391,793, aminoaluminosiloxanes as described in US-A 5,371,260, aminoaluminosiloxane hydrochlorides as described in EP-A 633 264, siloxyaluminosiloxanes as described in EP-A 621 279, or mixtures thereof.

35

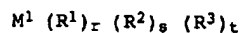
It has been found to be advantageous to use the metallocene complexes and the oligomeric aluminosiloxane compound in such amounts that the atomic ratio of aluminum from the oligomeric aluminosiloxane compound and the transition metal from the metallocene complexes is in the range from 10:1 to 10<sup>6</sup>:1, in particular in the range from 10:1 to 10<sup>4</sup>:1.

45



The catalyst system of the present invention may, if desired, further comprise, as component D<sub>1</sub>, a metal compound of the general formula I

5



I

where

10

M<sup>1</sup> is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table, i.e. boron, aluminum, gallium, indium or thallium,

15

R<sup>1</sup> is hydrogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, alkylaryl or arylalkyl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical,

20

R<sup>2</sup> and R<sup>3</sup> are hydrogen, halogen, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>15</sub>-aryl, alkylaryl, arylalkyl or alkoxy each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical,

25

r is an integer from 1 to 3

and

30

s and t are integers from 0 to 2, with the sum r+s+t corresponding to the valence of M<sup>1</sup>.

35 Among the metal compounds of the general formula I, preference is given to those in which

M<sup>1</sup> is lithium, magnesium or aluminum and

40 R<sup>1</sup> to R<sup>3</sup> are C<sub>1</sub>-C<sub>10</sub>-alkyl.

Particularly preferred metal compounds of the formula I are n-butyllithium, n-butyl-n-octylmagnesium, n-butyl-n-heptylmagnesium, tri-n-hexylaluminum, triisobutylaluminum,  
45 triethylaluminum and trimethylaluminum.



If the component D, is used, it is preferably present in the catalyst system in an amount of from 800:1 to 1:1, in particular from 500:1 to 50:1 (molar ratio of M<sup>1</sup> from I to transition metal M from IV).

5

The components A<sub>1</sub>, B<sub>1</sub>, C<sub>1</sub> and, if used, D<sub>1</sub> are used together as the catalyst system of the present invention.

10 The catalyst systems of the present invention are usually obtainable by a method similar to that described in EP-A 294 942.

A preferred preparation process for the catalyst systems of the present invention comprises the process steps

- 15 a) contacting a solution of a compound capable of forming metallocenium ions with a second solvent in which this compound is only sparingly soluble, in the presence of the support material,
- 20 b) removing at least part of the solvent from the support material and
- 25 c) contacting a solution of a mixture of a compound capable of forming metallocenium ions and a transition metal complex with a second solvent in which this mixture is only sparingly soluble, in the presence of the support material obtained as described in a) and b).

30 This preparation process is described in detail in the earlier German Patent Application 196 26 834.6, in particular page 12, line 15, to page 15, line 27, and examples, as well as in EP-A 295 312 which is cited in that Application.

35 The catalyst systems of the present invention are particularly suitable for preparing C<sub>2</sub>-C<sub>12</sub>-alk-1-ene polymers which are notable for, inter alia, a narrow molar mass distribution and very low proportions of xylene-soluble material. Owing to the very low proportions of xylene-soluble material, the C<sub>2</sub>-C<sub>12</sub>-alk-1-ene  
40 polymers, which are likewise the subject matter of the present invention, are particularly useful as packaging materials in the food sector.

The process of the present invention in which the catalyst  
45 systems described are used is relatively simple to carry out and gives a high productivity. The resulting polymers of C<sub>2</sub>-C<sub>12</sub>-alk-



1-enes can be processed to give, in particular, fibers, films and moldings.

#### Examples

5

#### Comparative Example A

#### I. Preparation of the support material

10

20 g of silica gel (particle diameter: 20 - 45  $\mu$ m; specific surface area: 280 m<sup>2</sup>/g; pore volume: 1.7 cm<sup>3</sup>/g; proportion by volume of voids and channels in the total particle: 15 %; pH: 7.0) were dehydrated under reduced pressure at 180°C for 8 hours, then suspended in 250 ml of toluene and subsequently admixed at room temperature with 160 ml of 1.53 M methylaluminumoxane (from Witco). After 12 hours, the silica gel deactivated with methylaluminumoxane was filtered off, washed twice with 100 ml each time of toluene and dried under reduced pressure. The yield was 27.9 g of silica gel-supported methylaluminumoxane.

#### II. Application of the catalyst to the support

25

4.9 g of the silica gel deactivated with methylaluminumoxane, as obtained under I., were slowly added to a mixture of 28 mg of bis[3,3'-(2-methylbenzo[e]indenyl)]dimethylsilane-diylzirconium dichloride, 6.3 ml of 1.53 M methylaluminumoxane solution (in toluene, from Witco) and 22 ml of toluene. After 30 minutes, the solvent was slowly removed in a controlled manner up to room temperature in a high vacuum. The yield of supported catalyst was 5.0 g.

#### 35 III. Polymerization of propylene

50 g of polypropylene powder followed by 10 ml of triisobutyl aluminum (2 molar in a heptane solution) were placed in a dry 10 liter autoclave flushed with nitrogen and stirred for 15 minutes. The reactor was subsequently charged in a countercurrent of nitrogen with 670 mg of the supported catalyst obtained in II. The reactor was closed again and then charged at room temperature with 1.5 l of liquid propylene at a stirrer speed of 350 rpm. After 45 prepolymerization for 30 minutes, the temperature was first increased to 65°C, with the internal pressure in the reactor being increased in stages by automatic pressure regulation to



a final pressure of 25 bar. Polymerization was subsequently carried out in the gas phase at 65°C for 90 minutes with automatic propylene gas regulation (25 bar). After polymerization was complete, the autoclave was depressurized to atmospheric pressure for 10 minutes and the resulting polymer was discharged in a stream of nitrogen. This gave 340 g of polypropylene powder, corresponding to a productivity of 650 g of polypropylene/g of catalyst/hour. The associated data for the polymer are listed in Table 1 below.

10

The particle diameter of the support was determined by Coulter Counter analysis (particle size distribution of the support particles), the pore volume and the specific surface area were determined by nitrogen absorption in accordance with DIN 66 131 or by mercury porosimetry in accordance with DIN 66 133. The mean particle size of the primary particles, the diameter of the voids and channels and their macroscopic proportion by volume were determined by means of scanning electron microscopy or electron probe microanalysis, in each case on grain surfaces and on grain cross sections of the support. The pH of the support was determined by the method of S.R. Morrison "The Chemical Physics of Surfaces", Plenum Press, New York [1977], page 130ff.

25 Comparative Example B

The procedure of Comparative Example A was repeated, but the supported catalyst was prepared on the basis of a granular, acid silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 320  $\text{m}^2/\text{g}$ ; pore volume: 1.75  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: < 5 %; pH: 5.5). In the polymerization of propylene, 830 mg of supported catalyst gave 1360 g of polymer powder, corresponding to a productivity of 1050 g of PP/g of catalyst/hour. The associated polymer data are listed in Table 1.

Example 1

40 The procedure of Comparative Example A was repeated, but the supported catalyst was prepared on the basis of an acid silica gel having an increased proportion by volume of voids and channels (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 5.5) In the polymerization of propylene, 445 mg of supported catalyst gave 1500 g of polymer powder, corresponding to a productivity of



2200 g of PP/g of catalyst/hour. The associated polymer data are listed in Table 1.

## Example 2

5

The procedure of Comparative Example A was repeated, but the supported catalyst was prepared on the basis of an acid silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %, pH: 5.0). In the polymerization of propylene, 445 mg of supported catalyst gave 1655 g of polymer powder, corresponding to a productivity of 2400 g of PP/g of catalyst/hour. The associated polymer data are listed in Table 1.

15

## Example 3

The procedure of Comparative Example A was repeated, but the supported catalyst was prepared on the basis of an acid silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 310  $\text{m}^2/\text{g}$ ; pore volume: 1.60  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 4.5). In the polymerization of propylene, 410 mg of supported catalyst gave 1620 g of polymer powder, corresponding to a productivity of 2550 g of PP/g of catalyst/hour. The associated polymer data are listed in Table 1.

20

25

## Example 4

30

The procedure of Comparative Example A was repeated, but the supported catalyst was prepared on the basis of an acid silica gel (particle diameter: 20-45  $\mu\text{m}$ , specific surface area: 315  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 8 %; pH: 5.0) In the polymerization of propylene, 565 mg of supported catalyst gave 1580 g of polymer powder, corresponding to a productivity of 1580 g of PP/g of catalyst/hour. The associated polymer data are listed in Table 1.

35

40

## Example 5

The procedure of Comparative Example A was repeated, but the supported catalyst was prepared on the basis of an acid silica gel (particle diameter: 20-45  $\mu\text{m}$ , specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and

45



channels in the total particle: 24 %; pH: 5.0). In the polymerization of propylene, 395 mg of supported catalyst gave 1650 g of polymer powder, corresponding to a productivity of 2700 g of PP/g of catalyst/hour. The associated polymer data are listed in Table 1.

## Comparative Example C

## 10 I. Preparation of the support material

12.1 g of silica gel (particle diameter: 20-45  $\mu$ m; specific surface area: 280 m<sup>2</sup>/g; pore volume: 1.56 cm<sup>3</sup>/g; proportion by volume of voids and channels in the total particle: 15 %; pH: 7.0) were suspended in 90 ml of heptane and thermostated to 20°C. 33.9 ml of a one molar solution of trimethylaluminum (TMA) in heptane were added over a period of 90 minutes, with the temperature not exceeding 40°C. After the TMA addition was complete, the mixture was stirred further for 4 hours. The suspension was filtered and the solid was washed twice with 20 ml each time of heptane. After drying at 50°C, the modified support remained as a free-flowing powder.

## 25 II. Application of the catalyst to the support

A solution of 131.3 mg of bis(n-butylcyclopentadienyl) zirconium dichloride in 56 ml of 1.53 M methylaluminoxane solution in toluene was stirred for 20 minutes and 12.6 g of the support modified as described in I. were then added at 20°C and the mixture was stirred further for 45 minutes. It was then filtered and the solid was subsequently washed twice with heptane. After drying at 50°C, 15.1 g of the supported catalyst was obtained as a free-flowing powder.

## 35 III. Polymerization of ethylene

A stirred 10 liter steel autoclave was carefully flushed with nitrogen and heated to the polymerization temperature of 70°C and then charged with 4.5 liters of isobutane and 80 mg/l of n-butyllithium. 365 mg of the supported catalyst obtained from II. were then rinsed in with a further 0.5 l of isobutane and the autoclave was pressurized with ethylene to a total pressure of 38 bar. The pressure in the autoclave was kept constant by metering in further ethylene. After 90 minutes, the polymerization was stopped by depressurizing the autoclave. 1660 g of polymer were obtained in the form of a



free-flowing powder. The corresponding polymerization results are listed in Table 2.

## Example 6

5

The procedure of Comparative Example C was repeated, but the supported catalyst was prepared on the basis of an acid silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 5.5). In the polymerization of ethylene, 265 mg of supported catalyst gave 1600 g of polymer powder, corresponding to a productivity of 4000 g of polyethylene (PE)/g of catalyst/hour. The associated polymer data are listed in Table 2.

15

## Example 7

The procedure of Comparative Example C was repeated, but the supported catalyst was prepared on the basis of an acid silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 305  $\text{m}^2/\text{g}$ ; pore volume: 1.48  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 5.5). In the polymerization of ethylene, 215 mg of supported catalyst gave 1500 g of polymer powder, corresponding to a productivity of 4600 g of PE/g of catalyst/hour. The associated polymer data are listed in Table 2.

20

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## Comparative Example D

30

The procedure of Comparative Example C was repeated, but the supported catalyst was prepared on the basis of a granular silica gel (particle diameter: 50  $\mu\text{m}$ ; specific surface area: 320  $\text{m}^2/\text{g}$ ; pore volume: 1.75  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: < 5 %; pH: 5.5). In the polymerization of ethylene, 440 mg of supported catalyst gave 1440 g of polymer powder, corresponding to a productivity of 2150 g of PE/g of catalyst/hour. The associated polymer data are listed in Table 2.

35

40

45





## Comparative Example E

## I. Application of the catalyst to the support

5 5 g of aluminum oxide having a pH of 7.5, a proportion by volume of voids and channels in the total particle of < 1.0 % and an activity value of 1 were slowly added to a 1.53 M solution of methylaluminoxane (from Witco) in 80 ml of  
10 toluene at 0°C. After 12 hours, the aluminum oxide was filtered off, washed twice with 100 ml each time of toluene and directly added slowly to a mixture of 28.5 mg of bis-[3,3'-(2-methylbenzo[e]indenyl)]dimethylsilanediyl-zirconium dichloride, 6.5 ml of a 1.53 M solution of  
15 methylaluminoxane in toluene and 25 ml of toluene. After 30 minutes, the solvent was removed slowly and in a controlled manner at room temperature in a high vacuum. This gave 5.1 g of a free-flowing powder as supported catalyst.

## 20 II. Polymerization of propylene

50 g of polypropylene powder were placed in a dry 10 liter autoclave flushed with nitrogen. Subsequently, 4 liters of liquid propylene, 10 ml of triisobutylaluminum (2 molar in  
25 heptane) and 975 mg of catalyst (obtained as described in I). were successively introduced into the reactor via a lock. At a stirrer speed of 350 rpm, the autoclave was charged at room temperature with a further 3 liters of propylene. The temperature was subsequently increased stepwise to 65°C, with  
30 an internal pressure of 26 bar being established. Polymerization was carried out for 90 minutes at 65°C. After polymerization was complete, the autoclave was depressurized to atmospheric pressure for 10 minutes and the polymer was discharged in the atom [sic] of nitrogen. This gave 255 g of  
35 polypropylene, corresponding to a productivity of 140 g of PP/g of catalyst/hour.

## Example 8

40 The procedure of Comparative Example E was repeated, but the catalyst was prepared on the basis of an acid aluminum oxide (pH = 4.5; activity: 1, proportion by volume of voids and channels in the total particle: 15 %). In the polymerization of  
45 propylene, 945 mg of supported catalyst gave 1050 g of polymer powder, corresponding to a productivity of 700 g of PP/catalyst/hour.



## Comparative Example F

## I. Preparation of the support material

5 250 g of silica gel (baked out under reduced pressure at 140°C for 7 hours) were suspended in 2000 ml of heptane and admixed with 350 ml of a 2 M solution of triisobutylaluminum in heptane. The silica gel was filtered off, washed with  
10 heptane and dried under reduced pressure. This gave the pretreated support as a free-flowing powder. This had a particle diameter of 20-45  $\mu\text{m}$ , a specific surface area of 320  $\text{m}^2/\text{g}$ , a pore volume of 1.75  $\text{cm}^3/\text{g}$ , a proportion by volume of voids and channels in the total particle of < 5.0 % and a pH of 7.0.

## II. Application of the catalyst to the support

A suspension of 0.5 mmol of dicyclopentadienylzirconium dichloride, 0.5 mmol of N,N-dimethylanilinium tetrakis-  
20 (pentafluorophenyl)borate and 5 g of silica gel pretreated as described in I. in 50 ml of toluene was heated to 80°C and stirred for 30 minutes at this temperature. The toluene was  
25 then distilled off under reduced pressure to give the supported catalyst as a free-flowing powder.

## III. Polymerization of ethylene

30 A stirred 10 liter steel autoclave was carefully flushed with nitrogen and heated to the polymerization temperature of 70°C and then charged with 4.5 liters of isobutane and 150 mg of butylheptylmagnesium. 280 mg of the catalyst supported as described in II. were then rinsed in with a further 0.5 l of  
35 isobutane and the autoclave was pressurized with ethylene to a total pressure of 38 bar. The pressure in the autoclave was kept constant by metering in further ethylene. After 90 minutes, the polymerization was stopped by depressurizing the autoclave. 160 g of polymer were obtained in the form of a  
40 free-flowing powder, corresponding to a productivity of 370 g of PE/g of catalyst/hour. The associated polymer data are listed in Table 3.

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## Example 9

The procedure of Comparative Example F was repeated, but the supported catalyst was prepared on the basis of a spray-dried silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 5.5). In the polymerization of ethylene, 68 mg of supported catalyst gave 200 g of polymer powder, corresponding to a productivity of 2000 g of PE/g of catalyst/hour. The associated polymer data are listed in Table 3.

## Comparative Example G

The procedure of Comparative Example F was repeated, the supported catalyst was prepared on the basis of a granular silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 320  $\text{m}^2/\text{g}$ ; pore volume: 1.75  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: < 5 %; pH: 7.0), but the metallocene component used was di-n-butylcyclopentadienyl-zirconium dichloride. In the polymerization of ethylene, 66 mg of supported catalyst gave 255 g of polymer powder, corresponding to a productivity of 2560 g of PE/g of catalyst/hour. The associated polymer data are listed in Table 3.

## Example 10

The procedure of Comparative Example F was repeated, the supported catalyst was prepared on the basis of a spray-dried silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 5.5), but the metallocene component used was di-n-butylcyclopentadienyl-zirconium dichloride. In the polymerization of ethylene, 81 mg of supported catalyst gave 420 g of polymer powder, corresponding to a productivity of 3500 g of PE/g of catalyst/hour. The associated polymer data are listed in Table 3.

## Comparative Example H

The procedure of Comparative Example F was repeated, the supported catalyst was prepared on the basis of a granular silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 320  $\text{m}^2/\text{g}$ ; pore volume: 1.75  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: < 5 %; pH: 7.0), but the



metallocene component used was dimethylsilylbis(1-indenyl)zirconium [sic] dichloride. In the polymerization of ethylene, 75 mg of supported catalyst gave 195 g of polymer powder, corresponding to a productivity of 1700 g of PE/g of catalyst/ hour. The associated polymer data are listed in Table 3.

## Example 11

10 The procedure of Comparative Example F was repeated, the supported catalyst was prepared on the basis of a spray-dried silica gel (particle diameter: 20-45  $\mu\text{m}$ ; specific surface area: 325  $\text{m}^2/\text{g}$ ; pore volume: 1.50  $\text{cm}^3/\text{g}$ ; proportion by volume of voids and channels in the total particle: 15 %; pH: 5.5), but the  
15 metallocene component used was dimethylsilylbis(1-indenyl)zirconium [sic] dichloride. In the polymerization of ethylene, 72 mg of supported catalyst gave 240 g of polymer powder, corresponding to a productivity of 2200 g of PE/g of  
20 catalyst/hour. The associated polymer data are listed in Table 3.

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Table 1

	Compara- tive Exam- ple A	Compara- tive Exam- ple B	Example 1	Example 2	Example 3	Example 4	Example 5
Productivity [g of polymer/g of catalyst/hour]	650	1050	2200	2400	2550	1800	2700
Proportion of xylene- soluble material *) [% by weight]	0.5	0.4	0.3	0.3	0.5	0.4	0.3
Melt flow index **) [g/10 min]	5.9	4.7	4.8	4.2	6.0	4.8	4.9
Proportion by volume of voids and channels in the total particle [%]	15	<5	15	15	15	8	24
pH of the inorganic oxide	7.0	5.5	5.5	5.0	4.5	5.0	5.0
Molar mass distribu- tion [ $M_w/M_n$ ] ***)	2.1	2.1	1.8	1.9	1.9	1.8	1.8

\*) determined in accordance with DIN ISO 1873

\*\*) in accordance with DIN ISO 1133, or ASTM D 1238, at 230°C and 2.16 kg

\*\*\*) determined by gel permeation chromatography



Table 2

	Comparative Example C	Example 6	Example 7	Compara- tive Exam- ple D	Compara- tive Exam- ple E	Example 8
Productivity [g of polymer/g of catalyst/hour]	3050	4000	4600	2150	140	700
Proportion by volume of voids and channels within the total particle [%]	15	15	15	<5	<1.0	15
Viscosity [ $\eta$ ] *)	3.69	3.73	3.82	3.79		
pH of the inorganic support	7.0	5.5	5.5	5.5	7.5	4.5
Molar mass distribution [ $M_w/M_n$ ] **)	2.3	1.9	2.0	2.3	2.3	2.0

\*) determined in accordance with DIN ISO 1628-3

\*\*) determined by gel permeation chromatography



Table 3

	Comparative Example F	Example 9	Compara- tive Exam- ple G	Example 10	Compara- tive Exam- ple H	Example 11
Productivity [g of polymer/g of catalyst/hour]	370	2000	2560	3500	1700	2200
Viscosity [ $\eta$ ] *)	4.34	4.04	4.20	4.03	3.54	3.82
Proportion by volume of voids and channels within the total particle [%]	<5	15	<5	15	<5	15
pH of the inorganic support	7.0	5.5	7.0	5.5	7.0	5.5
Molar mass distribution [ $M_w/M_n$ ] **)	2.3	1.9	2.2	1.9	2.3	2.0

\*) determined in accordance with DIN ISO 1628-3

\*\*) determined by gel permeation chromatography



Tables 1-3 show that the use of an inorganic support having a pH of from 1 to 6 and a macroscopic proportion by volume of voids and channels based on the total particle of from 5 to 30%, as in  
5 Examples 1-11 according to the present invention and in contrast to the Comparative Examples A-H, results in polymers having reduced proportions of xylene-soluble material. Furthermore, examples 1-11 according to the present invention exhibit  
10 significantly increased productivity.

Example 12

I. Preparation of the support material

15 100 g of granular silica gel (particle diameter: 20 - 45  $\mu$ m; specific surface area: 320 m<sup>2</sup>/g; pore volume: 1.75 cm<sup>3</sup>/g; channels in the total particle: <5%; pH: 5.5) were dehydrated under reduced pressure at 180°C for 8 hours, then suspended  
20 in 450 ml of toluene and subsequently admixed at room temperature with 775 ml of 1.53 M methylaluminoxane (in toluene, from Witco). After 12 hours, the silica gel deactivated with methylaluminoxane was admixed with 750 ml of isododecane and stirred at room temperature for a further 1.5 hours. The sup-  
25 port material was subsequently filtered off, washed twice with 150 ml each time of toluene and twice with 150 ml each time of pentane and dried in a nitrogen-fluidized bed. The yield was 146 g of silica gel deactivated with methylaluminoxane.

30 II. Application of the catalyst to the support

146 g of the silica gel deactivated with methylaluminoxane, as obtained under I., were added to a mixture of 5.25 g of  
35 bis[3,3'-(2-methylbenzo[e]indenyl)]dimethylsilane-diyl-zirconium dichloride, and 1.2 l of 1.53 M methylaluminoxane solution (in toluene, from Witco) were added and the mixture was stirred at room temperature. After 20 hours, 2.5 l of isododecane were added slowly and in a controlled manner over  
40 a period of 4 hours and the mixture was stirred at room temperature for a further 1.5 hours. The solid was subsequently filtered off, washed with 150 ml each time of pentane and dried in a nitrogen-fluidized bed. The yield of supported catalyst was 154 g. Si-content of the catalyst:  
45 25.42% by weight.





## Examples 13 to 15

## Polymerization in a continuous 200 l gas-phase reactor

The polymerizations were carried out in a vertically mixed gas-phase reactor having a utilizable volume of 200 l. The reactor contained an agitated fixed bed of finely divided polymer. The reactor output was in all cases 20 kg of polypropylene per hour. The polymerization results of Examples 13, 14 and 15 are listed in Table 4.

10

## Example 13

At 60°C and a pressure of 24 bar, liquid propylene was expanded into the gas-phase reactor. The catalyst from Example 12 was metered in together with the propylene added for regulating the pressure. The catalyst was metered in in such an amount that the mean output of 20 kg/h was maintained. Triisobutylaluminum (TIBA) was also metered in in an amount of 30 mmol/h as a 1 molar solution in heptane. Polymer was removed gradually from the reactor by briefly depressurizing the reactor via an immersed tube. The productivity was calculated from the silicon content of the polymer according to the following formula:

$$P = \text{Si content of the catalyst} / \text{Si content of the product}$$

25

The process parameters and characteristic product properties are shown in Table 4.

## Example 14

30

Example 13 was repeated except that hydrogen was added as molecular weight regulator. The hydrogen concentration in the reaction gas was determined by gas chromatography. The process parameters and characteristic product properties are shown in Table 4.

35

## Example 15

Example 13 was repeated except that 1-butene was metered into the reactor as comonomer. The butene concentration in the reaction gas was determined by gas chromatography. The process parameters and characteristic product properties are shown in Table 4.

45



## Example 16

## I. Preparation of the support material

- 5 100 g of silica gel (particle diameter: 20 - 45  $\mu$ m; specific surface area: 325 m<sup>2</sup>/g; pore volume: 1.50 cm<sup>3</sup>/g; channels in the total particle: 15%; pH: 5.0) were dehydrated under reduced pressure at 180°C for 8 hours, then suspended in 450 ml of toluene and subsequently admixed at room
- 10 temperature with 775 ml of 1.53 M methylaluminoxane (in toluene, from Witco). After 12 hours, the silica gel deactivated with methylaluminoxane was admixed with 750 ml of isododecane and stirred at room temperature for a further 1.5 hours. The support material was subsequently filtered
- 15 off, washed twice with 150 ml each time of toluene and twice with 150 ml each time of pentane and dried in a nitrogen-fluidized bed. The yield was 159 g of silica gel deactivated with methylaluminoxane.

## 20 II. Application of the catalyst to the support

- 159 g of the silica gel deactivated with methylaluminoxane, as obtained under I., was added to a mixture of 5.25 g of
- 25 bis[3,3'-(2-methylbenzo[e]indenyl)]dimethylsilanediyloxane zirconium dichloride, and 1.2 l of 1.53 M methylaluminoxane solution (in toluene, from Witco) were added and the mixture was stirred at room temperature. After 20 hours, 2.5 l of isododecane were added slowly and in a controlled manner over a period of 4 hours and the mixture was stirred at room
- 30 temperature for a further 1.5 hours. The solid was subsequently filtered off, washed with 150 ml each time of pentane and dried in a nitrogen-fluidized bed. The yield of supported catalyst was 165 g. Si content of the catalyst: 24.73% by weight.

35

Examples 17 to 19

Polymerization in a continuous 200 l gas-phase reactor

- The polymerizations were carried out in a vertically mixed
- 40 gas-phase reactor having a utilizable volume of 200 l. The reactor contained an agitated fixed bed of finely divided polymer. The reactor output was in all cases 20 kg of polypropylene per hour. The polymerization results from Examples 17, 18 and 19 are listed in Table 4.

45



## Example 17

At 60°C and a pressure of 24 bar, liquid propylene was expanded into the gas-phase reactor. The catalyst from Example 16 was  
5 metered in together with the propylene added for regulating the pressure. The catalyst was metered in in such an amount that the mean output of 20 kg/h was maintained. Triisobutylaluminum (TIBA) was also metered in in an amount of 30 mmol/h as a 1 molar solution in heptane. Polymer was removed gradually from the  
10 reactor by briefly depressurizing the reactor via an immersed tube. The productivity was calculated from the silicon content of the polymer according to the following formula:

$$P = \text{Si content of the catalyst} / \text{Si content of the product}$$

15

The process parameters and characteristic product properties are shown in Table 4.

## Example 18

20

Example 17 was repeated except that hydrogen was added as molecular weight regulator. The hydrogen concentration in the reaction gas was determined by gas chromatography. The process parameters and characteristic product properties are shown in  
25 Table 4.

## Example 19

Example 17 was repeated except that 1-butene was metered into the  
30 reactor as comonomer. The butene concentration in the reaction gas was determined by gas chromatography. The process parameters and characteristic product properties are shown in Table 4.

35

40

45



Table 4  
Results of the continuous polymerization experiments of Examples 13, 14, 15, 17, 18 and 19

	Example 13	Example 14	Example 15	Example 17	Example 18	Example 19
p/T [bar/°C]	24/60	24/60	24/60	24/60	24/60	24/60
TIBA [mmol/h]	30	30	30	30	30	30
H <sub>2</sub> [l/% by volume]	0	0.110	0	0	0.105	0
1-butene [% by volume]	0	0	4.6	0	0	4.5
Product data						
MFI [g/10'] <sup>a)</sup>	4.7	21.3	3.9	4.6	20.6	4.1
DSC [°C]	146.7	145.8	133.8	146.5	145.6	133.4
eta [dl/g]	2.17	1.57	2.28	2.19	1.55	2.27
XL [%]	0.4	0.5	0.4	0.4	0.5	0.5
Si [ppm]	41.00	28.40	44.59	20.02	16.49	20.78
Prod. [gPP/gKat]	6200	8950	5700	12,350	15,000	11,900

<sup>a)</sup> in accordance with ISO 1133



Examples 20, 20C, 21 and 21C

1. Spinning experiments

5

Examples 20, 20C

10 The spinning experiments were carried out on a spinning-drawing-texturing unit Barmag 4E/1-Rieter J0/10. The spinning temperatures were 240°C, the drawing ratio was 1:3.4 at a drawing speed of 2000 m/min. A titer of about dtex1220 f68 having a trilobal nozzle geometry was spun. A melt sieve packing of 6000/1500/300 mesh was installed upstream of the spinning nozzle. The initial pressure upstream of the sieve packing was 60 bar. The air flow velocity onto the fiber was 0.8 m/sec, the temperature of the air stream was 18°C and the preparation application was 0.8%. The spinning behavior and the fiber properties are shown in Table S1. Each of the spinning experiments was carried out using a metallocene homopolymer having a melt flow index of 20 g/10 min from Examples 14 (for Example 20C) and 18 (for Example 20).

Example 20C: Catalyst on granular silica gel as described in Example 12;

25 Example 20: Catalyst on spherical silica gel as described in Example 16.

Table S1

	Unit	Standard	Example 20C	Example 20
30 MFI 230°C/2.16 kg	g/10 min	ISO 1133	21.3	20.6
35 Spinning behavior	-		Continuous pressure rise upstream of the sieve packing, spinning and drawing breaks in the filaments	No pressure rise upstream of the sieve packing, no spinning and drawing breaks
Titer	dtex	DIN 53830	1216	1224
Strength	cN/dtex		1.95	2.14
Elongation	%		107	102
40 Uster <sup>a)</sup>	%		1.68	1.06

a) Determination of the nonuniformity (mass fluctuations) of multifilaments. The material to be tested runs through a measuring head which determines, by measuring the capacity, an instantaneous value proportional to the linear density (titer) of the filament. These instantaneous values are used for calculating an index for the percentage nonuniformity.

45



As can be seen from Table S1, the polypropylene from Example 20C displays significantly worse spinning and drawing behavior in terms of filament breaks and also worse filament properties such as low filament strength and a higher filament nonuniformity, expressed by the Uster value, in comparison with the polypropylene from Example 20.

## 2. Flat film experiment

### 10 Examples 21 and 21C

For the experiments, films were produced on a flat film unit. This comprised a 90 mm Barmag extruder having a 25 D screw with mixing section and an 800 mm Johnson die having a die slit of 0.5 mm. The temperatures in the extruder were from 210°C increasing to 255°C and the die temperature was 250°C. The cooling roller temperature was 20°C and the film takeoff velocity was 14 m/min at a throughput of 30 kg/h.

Each of the flat film experiments was carried out using a metallocene homopolymer having a melt flow index of 7 g/10 min, prepared by a method similar to Examples 14 and 18.

Example 21C: Catalyst on granular silica gel as described in Example 12;  
Example 21: Catalyst on spherical silica gel as described in Example 16

30 The film properties are shown in Table F2.

Table F2

Property	Standard	Unit	Example 21C	Example 21
35 MFI 230°C/2.16 kg	ISO 1133	g/10 min	7	7
Film thickness		µm	50	50
Strength: longitudinal transverse	ISO 527	N/mm <sup>2</sup>	39.9 38.9	40.1 39.2
40 Elongation: longitudinal transverse	ISO 527	%	750 760	760 770
E modulus: longitudinal transverse	DIN 53121	N/mm <sup>2</sup>	880 860	880 870
45 Haze after 7 days	ASTM D 1003	%	1.6	1.1
Gloss (20°C) after 7 days	ISO 2813	skt	107	113



36

As can be seen from Table F2, the films from Example 21 display better film properties, in particular better optical properties such as lower haze or higher gloss, than the films from Example 21C.

5

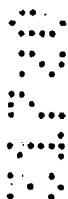
The results from Examples 12 to 21 show that the catalyst systems of the present invention have particularly good properties, for example high productivities, if they are obtained by the preparative process described in the earlier German Patent

10 Application 19626834.6. The polymers obtainable using these catalysts give, for example, fibers or films having, inter alia, good mechanical and optical properties.

"Comprises/comprising" when used in this specification is taken to

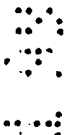
15 specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A catalyst system for polymerizing  $C_2-C_{12}$ -alk-1-enes, comprising
  - A, an inorganic support,
  - B, at least one metallocene complex,
  - C, at least one compound capable of forming metallocenium ions and
  - D, if desired, at least one organic metal compound of an alkali metal or alkaline earth metal or a metal of main group III of the Periodic Table,

wherein the inorganic support used is an inorganic oxide which has a pH of from 1 to 6 and voids and channels whose macroscopic proportion by volume based on the total particle is in the range from 5 to 30 %.

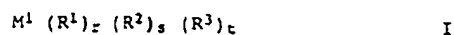
2. A catalyst system as claimed in claim 1, wherein the inorganic support A) has a pH of from 2 to 5.5 and voids and channels whose macroscopic proportion by volume based on the total particle is in the range from 8 to 30 %.
3. A catalyst system as claimed in claim 1 or 2, wherein the inorganic support has a mean particle diameter of from 5 to 200  $\mu m$ , a mean particle diameter of the primary particles of from 1 to 20  $\mu m$  and voids and channels having a mean diameter of from 0.1 to 20  $\mu m$ .
4. A catalyst system as claimed in any of claims 1 to 3, wherein the inorganic support is an oxide of silicon, of aluminum, of titanium or is an oxide of a metal of main group I or II of the Periodic Table.
5. A catalyst system as claimed in claim 4, wherein the inorganic support is silica gel ( $SiO_2$ ).

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6. A catalyst system as claimed in claim 5, wherein the silica gel ( $\text{SiO}_2$ ) used has been spray dried.
7. A catalyst system as claimed in any of claims 1 to 6, wherein a metallocene complex B, of titanium, zirconium or hafnium is used.
8. A catalyst system as claimed in any of claims 1 to 7, wherein the organic metal compound D, used is a metal compound of the general formula I,



where

$\text{M}^1$  is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table,

$\text{R}^1$  is hydrogen,  $\text{C}_1$ - $\text{C}_{10}$ -alkyl,  $\text{C}_6$ - $\text{C}_{15}$ -aryl, alkylaryl or arylalkyl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical,

$\text{R}^2$  and  $\text{R}^3$  are hydrogen, halogen,  $\text{C}_1$ - $\text{C}_{10}$ -alkyl,  $\text{C}_6$ - $\text{C}_{15}$ -aryl, alkylaryl, arylalkyl or alkoxy each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical,

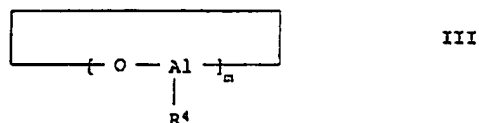
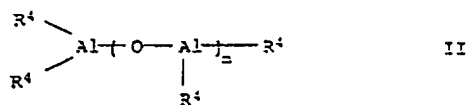
$r$  is an integer from 1 to 3

and

$s$  and  $t$  are integers from 0 to 2, with the sum  $r+s+t$  corresponding to the valence of  $\text{M}^1$ .

9. A catalyst system as claimed in any of claims 1 to 8, wherein compounds C, capable of forming metallocenium ions which are used are open-chain or cyclic aluminoxane compounds of the general formula II or III,





where  $\text{R}^4$  is a  $\text{C}_1$ - $\text{C}_4$ -alkyl group and  $m$  is an integer from 5 to 30.

10. A process for preparing polymers of  $\text{C}_2$ - $\text{C}_{12}$ -alk-1-enes at from  $-50$  to  $300^\circ\text{C}$  and pressures of from 0.5 to 3000 bar, wherein use is made of a catalyst system as claimed in any of claims 1 to 9.
11. A process as claimed in claim 10, wherein the polymerization is carried out in liquid monomers or in the gas phase.
12. A process as claimed in claim 10 or 11, wherein a prepolymerization is first carried out in suspension or in liquid monomers.
13. A process as claimed in any of claims 10 to 12, wherein propylene is used as  $\text{C}_2$ - $\text{C}_{12}$ -alk-1-ene.
14. A process as claimed in any of claims 10 to 12, wherein ethylene is used as  $\text{C}_2$ - $\text{C}_{12}$ -alk-1-ene.
15. A polymer of  $\text{C}_2$ - $\text{C}_{12}$ -alk-1-enes, obtained by a process as claimed in any of claims 10 to 14.
16. Use of a polymer of  $\text{C}_2$ - $\text{C}_{12}$ -alk-1-enes as claimed in claim 15 for producing fibers, films and moldings.
17. A fiber, film or molding obtained from the polymers of  $\text{C}_2$ - $\text{C}_{12}$ -alk-1-enes as claimed in claim 15.

DATED this 16th day of February 2000

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